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Volume A 28:

Water to Zirconium and Zirconium Compounds

Editors: Barbara Elvers, Stephen Hawkins

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## Cross Referer

Weed Killers →  
Weld Cladding  
Wheat → Cere  
Whey → Cheese  
Whisky → Spiri  
Wollastonite →  
Wood Gasificati  
Wood Pulp → P  
Xanthan Gum -  
Xanthene Dyes -  
Xenon → Noble

oxide and hydrogen) is bubbled through. At reaction temperatures of 220–240 °C and pressures around 2 MPa, *n*-alkanes and *n*-alkenes are formed preferentially, with up to 40 % crude wax in the synthesis product.

Crude wax is separated from the other products of synthesis by fractional condensation. The low-boiling constituents (gasoline and diesel fuel) are removed by distillation under atmospheric pressure, followed by vacuum distillation to separate the *soft waxes*. Besides *n*-alkanes, distillation bottoms also contain alkenes, hydrocarbons with hydroxyl and carbonyl groups, and colored components. For purification and stabilization, the bottom products are subjected to a hydrofining step employing a nickel catalyst to yield a white *hard wax* that is practically free of alkenes, aromatics, functional hydrocarbons, and sulfur compounds.

Soft waxes are also subjected to hydrogenation.

**Properties.** Fischer–Tropsch waxes consist essentially of *n*-paraffins with chain lengths between 20 and 50 carbon atoms. Products with an average molar mass of 400 g/mol are marketed as soft, and those with an average molar mass of 700 g/mol as hard waxes. The paraffins have a fine crystalline structure and, because of the narrow molar mass distribution, a small melting range and very low melt viscosities. Congealing point, density, and hardness increase with increasing mean molar mass. The low molar mass compared with polyolefin waxes is the reason for a certain displacability of the crystal layers relative to each other and, associated with this, the polishability.

Synthetic paraffins are fully compatible with refined waxes, polyolefin waxes, and most vegetable waxes. They are soluble at elevated temperature in the usual wax solvents (e.g., naphtha, turpentine, and toluene) to give clear solutions. Addition of 10–20 % synthetic paraffin to other waxes increases their congealing point and hardness without significantly influencing melt viscosity. In wax pastes, the tendency of Fischer–Tropsch waxes to form microcrystals increases solvent retention. Some typical data for Fischer–Tropsch waxes are listed in Table 20.

**Uses.** Fischer–Tropsch waxes are used in plastics processing as lubricants for poly(vinyl chloride) and polystyrene, as well as mold-release agents; as melting point improvers, hard-

Table 20. Typical properties of Fischer–Tropsch soft and hard paraffins

Characteristic	Sasol Wax M	Sasol Wax H2 Vestowax SP 1602
Drop point, °C		100–112
Needle penetration, 0.1 mm		1–3
Color	white	white
Molar mass, g/mol	400	700
Density (at 23 °C), g/cm <sup>3</sup>	0.94	0.94
Viscosity (120 °C), mPa · s	< 20	< 20

eners, and viscosity reducers in hot melts and candles; and, because of their good polishability, for the production of cleaning agents and polishes.

Micronized waxes improve the abrasion resistance of paints and printing inks.

*Oxidized waxes* containing fatty acids and fatty acid esters are produced from synthetic paraffin by oxidation and partial saponification. Major areas of application are as mold-release agents in plastics processing, in polishes and cleaning agents, and as auxiliaries in the textile and paper industries.

**Trade Names.** Fischer–Tropsch waxes are marketed, e.g., as Sasol Wax (Sasol Marketing Co., Johannesburg, South Africa) and Vestowax SH/SP (Höls AG, Marl, Germany).

## 6. Polyolefin Waxes

### 6.1. Production and Properties

#### 6.1.1. Polyethylene Waxes by High-Pressure Polymerization

High-pressure polyethylene (PE) waxes are produced, like high-pressure polyethylene plastic, at high pressure and elevated temperature in the presence of radical formers. As waxes, their molar masses are considerably lower than those of plastics. The molar mass range is adjusted during polymerization by the addition of regulators.

High-pressure polyethylene waxes are partially crystalline and therefore consist mainly of branched molecular chains in which shorter side chains, such as ethyl and butyl, predominate.

They generally have polyethylene wax branched polyethylene tailinity and density waxes, HDPE waxes increasing the pressure

High-pressure par masses between [weight-average mol gel permeation chromatography] dominate the

The development proceeded in parallel (→ Polyolefins, A2) waxlike ethylene polymer a variant of the IC process [6.1]. In pressure ethylene waxes [6.2], [6.3]. Parallel thermal depolymerization of polyethylene waxes—was developed

With the rapid growth the expansion of production the economic importance increased rapidly. Waxery profiles could be density and molar mass and functionalizing

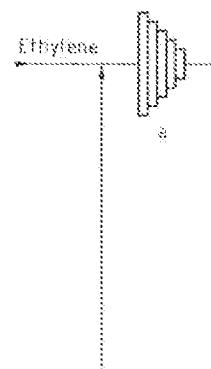


Figure 10. Schematic of a) Precompressor; b) P

They generally have low densities (low-density polyethylene waxes, LDPE waxes). Less branched polyethylene waxes with higher crystallinity and density (high-density polyethylene waxes, HDPE waxes) can be produced by increasing the pressure.

High-pressure polyethylene waxes with molar masses between 3000 and 20000 g/mol [weight-average molar mass  $\bar{M}_w$ , determined by gel permeation chromatography (GPC)] currently dominate the market.

The development of high-pressure PE waxes proceeded in parallel to that of LDPE plastics ( $\rightarrow$  Polyolefins, A21, pp. 488–489). In 1939, waxlike ethylene polymers were formed by using a variant of the ICI high-pressure polymerization process [6.1]. Industrial production of high-pressure ethylene waxes was started in the 1940s [6.2], [6.3]. Parallel to this, the technology of thermal depolymerization—the thermal degradation of polyethylene plastics to polyethylene waxes—was developed (see Section 6.1.4).

With the rapid growth of petrochemistry and the expansion of polyethylene plant capacities, the economic importance of PE waxes also increased rapidly. Waxes with very versatile property profiles could be synthesized by varying the density and molar mass of the homopolymers and functionalizing polyethylene by copolymer-

ization with various monomers (e.g., vinyl acetate or acrylic acid) or by melt oxidation.

Because PE waxes are rather inexpensive, have improved applicability and consistency in quality, and are in constant supply they have displaced expensive natural waxes (e.g., carnaúba and montan waxes) in many areas.

The high-pressure process is not applicable for production of polypropylene waxes, because only soft or oily products can be obtained. These waxes are therefore produced by the Ziegler process (see Section 6.1.3) or by depolymerization of high-density polypropylene (see Section 6.1.4).

#### 6.1.1.1. Production

The technology involved in the production of high-pressure PE waxes (see Fig. 10) is analogous to that used for high-pressure polyethylene ( $\rightarrow$  Polyolefins, A21, pp. 506–509). The only differences are in the product finishing process. Unlike viscous plastic melts, which must be granulated underwater in granulators, for example, the mobile wax melt can be converted into powder by spraying or into granules by using dicers.

The reaction vessels are stirred autoclaves or tubular reactors ( $\rightarrow$  Polyolefins, A21, pp. 507–508), the design of which can vary considerably.

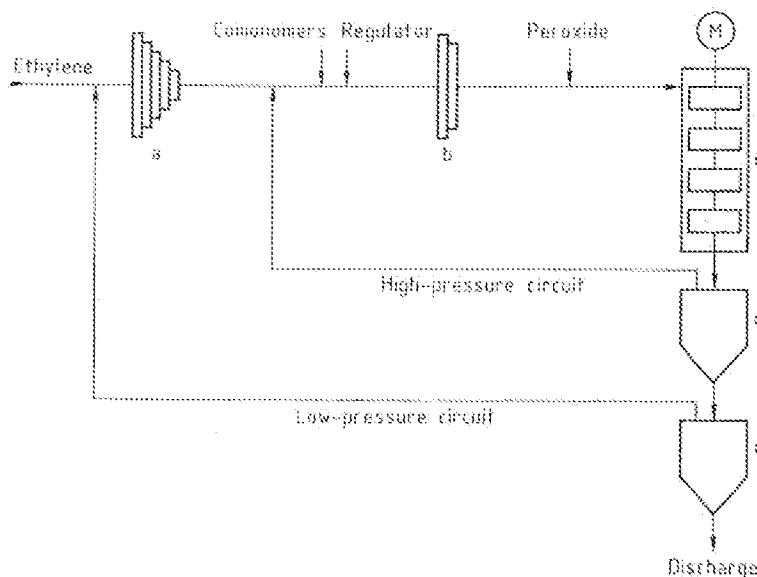
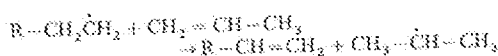
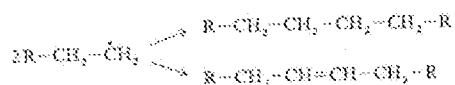


Figure 10. Schematic of production of polyethylene waxes by the high-pressure process in stirred autoclaves  
a) Precompressor; b) Postcompressor; c) Autoclave reactor; d) High-pressure separator; e) Low-pressure separator

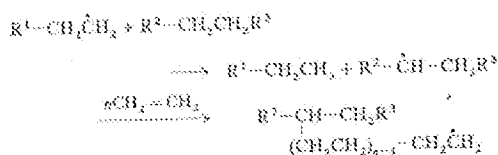
**Reaction Mechanism.** The high-pressure polymerization of ethylene is a highly exothermic radical chain reaction ( $\rightarrow$  Plastics, General Survey, A20, pp. 579-583), which is initiated by reaction of ethylene with radicals formed by decomposition of an initiator [6.4]. Chain propagation occurs through addition of further ethylene units. Chain growth is terminated, for example, by reaction with a regulator molecule such as propene:



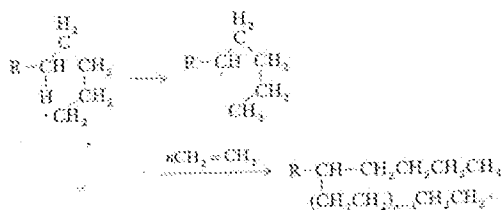
Polymerization is terminated by recombination or disproportionation of two macroradicals:



Long-chain branching occurs by intermolecular chain-transfer reactions:



A particular feature of polyethylene wax synthesis by the high-pressure process is the increased formation of short ethyl and butyl side chains. These are formed by intramolecular radical transfer:



At the high pressures necessary for polymerization, ethylene is in a supercritical state. Polymerization therefore takes place in a one-phase system. After leaving the reactor, the reaction mixture is decompressed in high- or low-pressure separators, and unreacted ethylene evaporates. The wax remains as a melt and ethylene is recycled.

**Reaction Conditions.** The structure, molar mass, and thus properties of polyethylene wax are determined mainly by reaction pressure, reaction temperature, type and quantity of initiator and molar mass regulator, and reactor type and geometry [6.5]-[6.9].

In the homo- and copolymerization of ethylene the reaction pressure is usually 150-320 MPa. Somewhat lower pressures are used in autoclaves than in tubular reactors. Other process variants involve much lower pressures of 70 MPa (max.) with isopropanol as the molar mass regulator [6.7], [6.8].

Higher pressure favors chain propagation and thus leads to very short residence times in the reactor. It also inhibits chain-transfer reactions so that with increasing pressure the degree of branching decreases and the density, crystallinity, hardness, and *mp* increase. In tubular reactors, rising pressure increases the polymer yield, whereas in autoclaves this effect is smaller.

For homopolymerization the reaction temperature is 200-350 °C and for copolymerization 200-300 °C. High reaction temperature favors chain-transfer reactions. For this reason the polyethylene waxes formed have many short-chain and only a few long-chain branches [6.10] and thus low densities. Higher-density waxes with lower degrees of branching are formed at lower reaction temperature.

Organic peroxides and molecular oxygen (the latter exclusively in tubular reactors) are used as initiators. They decompose into radicals under polymerization conditions. To ensure that the peroxides are metered reproducibly, they are dissolved in organic solvents.

Hydrogen and almost all organic compounds can act as molar mass regulators (chain terminators). Hydrogen, lower alkanes (e.g., propane), lower alkenes (e.g., propene or butene), alkyl aromatics, lower aldehydes (e.g., propionaldehyde), and lower alcohols (e.g., isopropanol) or mixtures of these substances are mainly employed. The concentration and reactivity of these regulators determine the average molar mass, the degree of branching, and thus the density of polyethylene wax. The activity of the regulator increases with increasing temperature and decreases with increasing pressure [6.4].

Reactor type and geometry also significantly influence polymer structure and properties. Because of the backmixing occurring in autoclaves, spherical molecules with many long-chain branches are predominantly formed. In tubular reac-

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tors with plug flow, long, straight molecules with little long-chain branching predominate [6.11]. High-density, highly crystalline polyethylene waxes can therefore be produced only in tubular reactors.

Just as the geometries of the autoclave and the tubular reactor differ, so do operating procedures. In the case of autoclaves the initiator solution and the molar mass regulator are charged directly to the preheated pressurized vessel by using high-pressure pumps. In tubular reactors the initiator (e.g., air) and the molar mass regulator are added to the reaction mixture before the compression stage or at the entrance to the reactor. With autoclaves, comonomers can be charged to different parts of the reaction vessel (see Fig. 10).

**Product Finishing.** Shaping of the molten polyethylene can be performed directly after removal of gaseous products in high- and low-pressure separators and subsequent fine degassing and filtration. Since no metal-containing catalysts are used in high-pressure polymerization of ethylene, no catalyst removal is necessary. Low molar mass fragments and residues of the initiator and molar mass regulator evaporate mainly in the separators. Only an extremely small proportion is incorporated into the polymer.

**Granules** can be produced by using strip dicers. The wax melt flows in thin strips on a continuous, water-cooled metal band and, after solidification, is chopped with a rotating knife. **Pastilles** can be obtained by metered dripping of the melt from a distributor head onto this type of cooling band.

A particular characteristic of wax melts is their low melt viscosity. Thus, spraying the melt to form **powders** of spherical particles is also possible. By using special nozzle arrangements (binary nozzles) with nitrogen as the atomizing gas, **miconized waxes** (very fine powders) with particle sizes in the micrometer range can be produced.

Powders and micronized waxes can also be obtained by grinding granules in jet mills. With soft or very viscoelastic waxes, cooling with dry ice or liquid nitrogen is necessary. Coarse particles must be removed by subsequent classification.

Like all organic dusts (e.g., coal or flour), wax powders, and particularly micronized waxes, are highly susceptible to dust explosions.

Appropriate safety precautions must be taken during processing, in particular grounding all installations to avoid spark formation through electrostatic charge buildup.

### 6.1.1.2. Properties

The transition from polyethylene plastic to polyethylene wax is flexible. If the molar mass is lowered, the thermoplastic material is gradually changed to a wax. The DGF definition of wax (see Section 1.2) gives an approximate boundary: For waxes, an upper limit to the melt viscosity of ca. 20 000 mm<sup>2</sup>/s at 120 °C is defined, which corresponds to an average molar mass (weight-average molar mass  $\bar{M}_w$ ) of ca. 37 000 g/mol.

The properties of polyethylene waxes are determined strongly by  $\bar{M}_w$  as a measure of the average chain length and by the degree of branching as a measure of the shape of the molecules. Melt viscosity increases with increasing molar mass. Crystallinity, hardness, *mp*, and solidification point increase as the degree of branching decreases. These data are important for application-oriented properties.

The molar mass can be determined by GPC. This method gives the weight-average ( $\bar{M}_w$ ) and the number-average ( $\bar{M}_n$ ) molar mass. The ratio  $\bar{M}_w/\bar{M}_n$  is a measure of molar mass distribution and is known as the polydispersity index ( $\rightarrow$  Polymerization Processes, A21, p. 314). For high-pressure polyethylene waxes currently produced, this value lies between 2.0 and 2.5. The waxes have a much narrower molar mass distribution than high-pressure polyethylene, for which the values are 3–8 (tubular reactor) and 12–16 (autoclave) [6.4].

Table 21 gives a series of structure and property data for three high-pressure polyethylene waxes with increasing density from two different producers (some of this represents unpublished data supplied by the authors).

The following conclusions can be drawn from these data:

- 1) The degree of branching is generally low with ca. ten branches (max.) per molecule. The side chains are mostly ethyl and butyl groups with a very small proportion of long-chain branches [6.12]–[6.14].
- 2) The density, crystallinity, hardness, solidification point, and drop point increase as degree of branching decreases [6.15]. All densi-

Table 21. Structure and properties of high-pressure polyethylene waxes A-C and D-F from two different producers

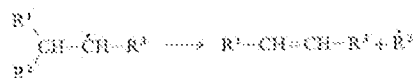
Characteristic	A	B	C	D	E	F
Density (23°C), g/cm <sup>3</sup> (DGF-M-III 2a)	0.92	0.92	0.945	0.92	0.92	0.94
CH <sub>2</sub> per 1000 C atoms	26	22	17	32	23	20
Branches per molecule	3.4	1.8	1.0	3.7	1.9	1.8
Crystallinity (from IR data), %	54	59	67	52	62	64
Central double bonds per 1000 C atoms	0.1	0.4	0.4	0	0	0
Terminal double bonds per 1000 C atoms	0.1	0.1	0	1.3	1.2	1.3
Side-chain double bonds per 1000 C atoms	0.6	0.4	0.2	0.9	0.5	0.4
Ball indentation hardness (23°C), bar (DGF-M-III 9a)	200	170	550	314	413	482
Solidification point, °C (DGF-M-III 4a)	98	99	106	93	101	104
Drop point, °C (DGF-M-III 3)	106	112	116	106	111	113
Melt viscosity (120°C), mm <sup>2</sup> /s (DGF-M-III 8)	1310	1160	1300	780	925	896
Weight-average molar mass $\bar{M}_w$ , g/mol	6140	5930	6000	5200	5500	5500
Number-average molar mass $\bar{M}_n$ , g/mol	2920	2390	2440	2490	2380	2660
$\bar{M}_w/\bar{M}_n$ (polydispersity index)	2.1	2.5	2.5	2.1	2.3	2.1

Table 22. Physical and chemical data for copolymeric high-pressure polyethylene waxes

Characteristic	Ethylene-vinyl acetate copolymer wax	Ethylene-acrylic acid copolymer wax
Weight-average molar mass $\bar{M}_w$ , g/mol	ca. 6800	ca. 6100
Number-average molar mass $\bar{M}_n$ , g/mol	3000	3000
Melt viscosity (120°C), mm <sup>2</sup> /s (DGF-M-III 8)	2000	1300
Solidification point, °C (DGF-M-III 4a)	85	93
Drop point, °C (DGF-M-III 3)	96	102
Ball indentation hardness (120°C), bar (DGF-M-III 9a)	120	410
Acid number, mg KOH/g		45
Vinyl acetate content, %	10	

ty-dependent properties vary correspondingly.

- 3) High-pressure PE waxes contain a small proportion of double bonds, whose distribution in the macromolecule depends on the production process, as the large differences between the levels of central double bonds show. The formation of double bonds is attributed to depolymerization of chain radicals at high reaction temperature [6.4], [6.16], e.g.:



High-density polyethylene waxes are colorless, white to transparent and form clear melts. Like other waxes, they dissolve in nonpolar solvents (e.g., aliphatic, aromatic, and chlorinated hydrocarbons) on heating and generally crystallize as very fine particles on cooling. Depending on the type and concentration of the wax, they then form mobile dispersions or paste-like gels, which frequently exhibit thixotropic properties.

### 6.1.2. Copolymeric Polyethylene Waxes by High-Pressure Polymerization (→ Polyolefins, A21, pp. 508–509)

In the high-pressure process, many other monomers can copolymerize with ethylene giving rise to considerable changes in product properties [6.7], [6.9]. For copolymerization, autoclaves with their intensive mixing, constant temperature, and consequently stable reaction process are particularly suitable. In industry, vinyl acetate and acrylic acid are used mainly as comonomers, giving waxes with higher polarity and lower crystallinity. Here also, the degree of branching decreases with increasing pressure and decreasing temperature. Density, *mp*, and hardness increase accordingly.

Table 22 gives characteristic data for two important copolymeric high-pressure polyethylene waxes with vinyl acetate and acrylic acid as comonomers.

Ethylene-vinyl acetate copolymer is a relatively polar but nevertheless hydrophobic wax that can be dispersed in organic solvents particu-

larly well. It is an automotive paint pigment concentrate hot melts.

Ethylene-acrylic acid copolymer is readily soluble in water for aqueous systems and is effective in emulsions for floor polishes and

### 6.1.3. Polyolefin Polymerization

Like high molecular weight polyethylene waxes can be produced by the high-pressure process (→ Polyolefins, A to the radical polymerization process). Like high molecular weight polyethylene waxes have a maximum melting point. They can contain small amounts of comonomers like high-pressure polyethylene.

For direct synthesis of propylene or high-pressure polyethylene process is possible (pp. 522–529).

Ziegler PE waxes have a molar mass ( $\bar{M}_n$ ). They thus belong to the thermoplastics. Besides the polymerization process, the degree of crystallinity of high-melting products with low molecular weight is low.

The soluble, low-melting waxes produced in the Ziegler process are more similar to normal hard waxes because of their high molecular weight only after process [6.17].

#### 6.1.3.1. Product

For the production of olefin waxes, Ziegler catalysts with low average chain-length distribution are active under the conditions of polymerization, carrying out poly-

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larly well. It is used as an additive in metallic automotive paints, as a dispersing agent in pigment concentrates, and as a component of hot melts.

*Ethylene-acrylic acid copolymer* is suitable for aqueous systems because it can be emulsified readily and is chemically and thermally intensive. Its emulsions are used mainly in modern floor polishes and mold-release agents.

### 6.1.3. Polyolefin Waxes by Ziegler-Natta Polymerization

Like high molar mass polyethylene plastics, PE waxes can be produced by the Ziegler low-pressure process using organometallic catalysts ( $\rightarrow$  Polyolefins, A21, pp. 509-511), in addition to the radical process at high pressure and temperature. Like high-density polyethylene, Ziegler waxes have a mainly linear molecular structure. They can contain short side chains but not long ones like high-pressure polyethylene waxes.

For direct synthesis of polymer waxes from propylene or higher  $\alpha$ -olefins, only the Ziegler-Natta process is suitable ( $\rightarrow$  Polyolefins, A21, pp. 522-529).

Ziegler PE waxes currently on the market have a molar mass between 800 and 8000 g/mol ( $M_n$ ). They thus bridge the gap between Fischer-Tropsch and paraffin waxes and HDPE thermoplastics. Besides controlling chain length, the polymerization process allows adjustment of the degree of crystallinity so that both hard-brittle, high-melting products and softer, flexible products with low melting points can be obtained.

The soluble, soft wax fractions inevitably produced in the suspension process for HDPE are more similar to paraffin waxes than to PE waxes because of their low molar masses. For normal hard wax applications, they can be used only after processing by distillation or extraction [6.17].

#### 6.1.3.1. Production

For the production of Ziegler-Natta polyolefin waxes, Ziegler catalysts that give polymers with low average chain lengths and narrow chain-length distributions, and are sufficiently active under the special conditions of wax synthesis, are particularly suitable. The low degree of polymerization typical of waxes is achieved by carrying out polymerization in the presence of

hydrogen as a molar mass regulator at comparatively high temperature (usually between 160 and 200 °C, sometimes even higher) [6.18]-[6.22]. Aliphatic hydrocarbons are used as reaction medium. Because of the high reaction temperature the waxes are formed in solution (solution polymerization). If the product viscosity is sufficiently low the molten polymer formed can itself function as the solvent (bulk polymerization) [6.23], [6.24]. Unlike modern HDPE processes in which the catalyst is not removed, in the case of wax synthesis the catalyst must usually be decomposed and filtered off [6.25], [6.26]. This applies at least to the heterogeneous titanium catalysts still used today (see below) and is necessary because waxes have higher purity requirements than PE plastics as a consequence of the applications for which they are used. After the solvent has been distilled off, the wax melt is shaped (e.g., by spraying or pastille formation).

**Catalyst Systems.** Classical Ziegler catalysts, consisting of titanium tetrachloride and alkylaluminum compounds, can be used for wax synthesis, but their activity is low [6.23], [6.24], [6.27]-[6.29]. The degree of branching and thus also the density, drop point, and hardness can be adjusted by copolymerization, by the special type of catalyst preparation [6.28], and by varying the polymerization temperature [6.23], [6.29].

The state of the art for production of *PE homo- and copolymer waxes* involves, as in plastics production, the use of supported catalysts, which contain titanium atoms as the active species and magnesium compounds as the carrier material ( $\rightarrow$  Polyolefins, A21, p. 503). Catalysts derived from titanium tetrachloride and magnesium chloride, oxide, hydroxide [6.19]-[6.22], or alkoxide [6.18], for example, are suitable.

Catalysts based on Ti-Mg compounds can also be used in the production of *polypropylene waxes*. Through an appropriate choice of catalyst, the degree of crystallinity (isotacticity) ( $\rightarrow$  Polyolefins, A21, pp. 532-534) can be varied within wide limits and thus adapted to a particular application. Flexible products with average crystallinity can be obtained [6.30]. Highly crystalline polypropylene waxes can now be produced economically by using stereoregulating silanes as additional catalyst components [6.31], [6.32]. Formerly, these waxes could be produced only by thermal degradation of high molar mass polypropylene (Section 6.1.4).



5           The ethylene acid-containing copolymer aqueous dispersion of the present invention consists essentially of a dispersion of component (A), an ethylene-methacrylic acid copolymer containing 15-35 wt% of methacrylic acid as the ethylene acid-containing copolymer, in water in the presence of component (B), ammonia used as a basic component in an amount greater than the amount of  
10   the carboxyl groups of component (A).

Both good dispersion property and good dispersion stability can be obtained by using an excess of component (B) ammonia, particularly an amount sufficient for neutralizing 110-150% of the carboxyl groups of the above-mentioned acid-containing copolymer (A). The resulting aqueous dispersion can  
15   be coated onto a substrate, such as a film, to make a coated substrate, particularly a coated film, that is not susceptible to moisture accumulation and has a good waterproofness.

It is suitable for ethylene-methacrylic acid copolymer (A) to contain 15-35 wt% or alternatively 15-25 wt%, particularly 18-30 wt%, of an  
20   unsaturated carboxylic acid. In the case of using a copolymer containing an unsaturated carboxylic acid in an amount that is less than the above-mentioned range, it is difficult to obtain a composition having a good aqueous dispersion property. In the case of using a copolymer containing an unsaturated carboxylic acid in an amount that is more than the above-mentioned range, a stable  
25   dispersion composition cannot be obtained and both the waterproofness and mechanical strength of the coated film are reduced.

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An ethylene-methacrylic acid copolymer having a melt flow rate of 50-2000 grams/10 minutes, particularly 60-1500, at 190°C/2160 gram load is suitable. In the case of using a methacrylic acid copolymer having an extremely  
30   low melt flow rate, an aqueous dispersion composition having a good dispersion property cannot be obtained. When using a copolymer having an excessively high melt flow rate, the coated film has a poor strength.

Besides ethylene and methacrylic acid, the copolymer may be copolymerized with other monomers including an unsaturated carboxylic acid  
35   ester such as methyl acrylate, ethyl acrylate, n-butyl acrylate, isobutyl acrylate, methyl methacrylate, isobutyl methacrylate, dimethyl maleate, or diethyl maleate; a vinyl ester such as vinyl acetate or vinyl propionate; and carbon monoxide, in an amount of 20 wt% or less, particularly 10 wt% or less.

The aqueous dispersion composition of the present invention  
40   contains ammonia, which can neutralize an excess, particularly 110-150%, more particularly 120-140% of the carboxyl groups of copolymer (A), along with copolymer (A).